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Thermodynamic properties of Ti–Al intermetallics

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Abstract

Thermodynamic properties of the titanium–aluminum system have been investigated over the entire composition range. A solid-state reversible galvanic cell employing a calcium fluoride (CaF_2) solid electrolyte and an Al–$CaAlF_7$ reference electrode was used in the temperature range 820–900 K for solid alloys containing 31.3, 47.9, 64.7, 73.6 and 99.0 atom percent aluminum. Experimental results of the activities of Al in the alloys showed a large negative deviation from ideal behavior. For instance the activity of Al in an alloy with 0.48 atomic fraction of Al was determined to be 2.98×10^{-3} at 850 K. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ti–Al alloys; Intermetallics; Thermodynamics; EMF

1. Introduction

Titanium-based intermetallics are gaining more popularity due to their excellent properties. The combination of light weight and high strength makes Ti-based alloys very attractive for aerospace and automotive industries. The demand for such alloys is on the rise as a result of increasing need for more sophisticated materials for various high-temperature applications. However, the alloys containing low Al content are brittle and provide moderate resistance to oxidation at the service temperatures. Alloying elements such as Nb, V, Cr, and Mn are added to these materials to enhance their ductility, strength, and oxidation and corrosion resistance.

Numerous studies on the phase diagram of the Ti–Al system are found in literature. The methods used to calculate the phase diagram differ and some discrepancies still remain. Murray [1] calculated the phase diagram by optimization of Gibbs energies with respect to phase diagram and thermochemical data. Kattner et al. [2] developed a phase diagram from calculations based on a least-squares technique to optimize the thermodynamic quantities of the analytical description using experimental data available in literature.

Solid-state galvanic cells have been widely used for thermodynamic measurements on systems in the solid phase. Solid state galvanic cell technique, commonly called electromotive force (EMF) method, is an accurate and useful method of generating thermodynamic data for systems in both solid and liquid phases. Calcium fluoride is a popular choice of electrolyte because its fluoride ion conductivity is close to unity over a wide range of temperatures [3,4]. Samokhval et al. [5] investigated the Ti-rich half of the Ti–Al binary system in the temperature range 890–1010 K. The experimental set-up and procedure used in the present study are similar to those used by them.

In the present investigation, a solid state galvanic cell technique was used employing CaF_2 as the electrolyte and Al–Ca_2AlF_7 as the reference electrode to obtain the thermodynamic data for the Ti–Al system. Various compositions corresponding to the intermetallics Ti_3Al, TiAl, $TiAl_2$, and $TiAl_3$ were studied.

The cell used in this study is of the form:

$$\mathrm{Pt,\ gr/Al,\ Ca_2AlF_7\|CaF_2\|Al\ (Ti{-}Al\ alloy),}$$
$$\mathrm{Ca_2AlF_7/gr,\ Pt}\quad \mathrm{(I)}$$

The half-cell reactions for the cell (I) can be written as follows:

$$\mathrm{Al(s) + 2CaF_2 + 3F^- = Ca_2AlF_7 + 3e^-}$$
$$\text{at left/reference electrode}$$
$$\mathrm{Ca_2AlF_7 + 3e^- = Al\ (Ti{-}Al\ alloy) + 2CaF_2 + 3F^-}$$
$$\text{at right/working electrode}$$

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Thus the overall cell reaction of the cell is given by:

Al(s) = Al (Ti–Al alloy)

2. Experimental

The electrolyte used was optical-grade calcium fluoride single crystal. Reference electrodes were produced by mixing 840 mg of CaF_2 with 360 mg of AlF_3 and 800 mg of Al powder. Powders were well mixed in a glove box under slight vacuum. The mixtures were cold pressed at 10 000 p.s.i. and then hot pressed at 900°C and 5000 p.s.i. for 30 min to form pellets (1 p.s.i. = 6894.76 Pa). The pellets were then sealed in a quartz tube under slight vacuum while passing argon and annealed at 600°C for 10 days. Working electrodes were prepared in the same way as reference electrodes. The only difference is that working electrodes contained 800 mg of titanium and aluminum powders in amounts to give the desired composition of the alloy.

After annealing, the samples were polished and prepared for X-ray diffraction (XRD) analysis as well as electron probe microanalysis (EPMA). This step is taken to ensure that the desired alloy was obtained without any undesirable phases such as oxides. The surfaces of the samples were ground smooth to ensure good cell contact prior to loading into the cell. The temperature was set to the desired value and the cell was held at this temperature for days to equilibrate. The cell temperature was controlled to ±0.5°C and the cell voltage was considered stable when the change in voltage was within 1 mV over a period of a few hours.

Fig. 1 shows an overview of the experimental set-up used. A vertical resistance furnace with a water-cooled brass end cap was used. A vacuum pump was connected to the system to apply a slight vacuum while ultra high-purity argon gas was passed at a flow rate of about 10–20 ml/min. Since oxidation is highly undesirable, efforts were made to prevent any possible leakage or air contamination in the set-up. The top of the furnace was well sealed with rubber o-ring and high-vacuum grease. Argon gas used in the experiments was first passed through a gettering furnace containing copper turnings held at about 600°C. In addition, copper turnings were also placed at the bottom of the reaction chamber to further purify the gas. The cell was placed in a constant-temperature zone of the furnace. The reaction temperature was controlled to ±0.5°C using Omega CN 76000 auto-tune controller. The cell voltage was measured using Keithley 610C solid-state electrometer. Both the temperature and the cell voltage were recorded in a computer using a data acquisition system.

Fig. 2 shows a schematic diagram of the cell assembly. The reaction chamber is an alumina tube. A rubber o-ring in the end cap provided a vacuum tight seal when the cell assembly was placed in the reaction tube. Argon gas was introduced at the bottom of the chamber. Inside the tube, two stainless steel plates were used to hold the samples together in the cell. A support rod was used on top of the cell to maintain contact between the electrolyte and electrodes. Between the two plates, the CaF_2 electrolyte was placed at the center of the cell. The electrolyte was surrounded by an electrode, a graphite thin film, a platinum disk, and an alumina wafer disk on each side. The purpose of the graphite thin films was to prevent any reaction between the platinum disks and the electrodes while maintaining good conductivity. The alumina wafers were

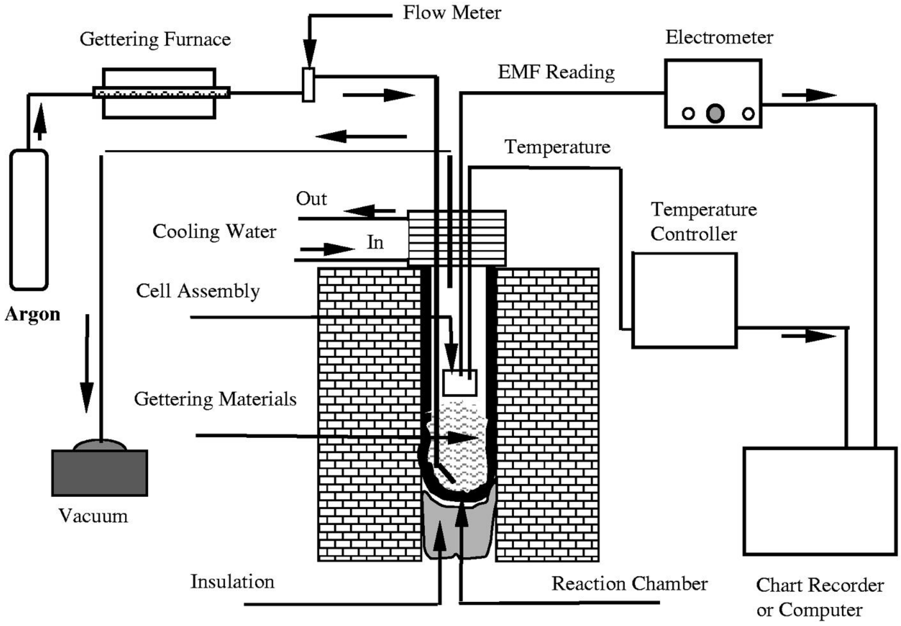

Fig. 1. Schematic diagram of the experimental set-up.

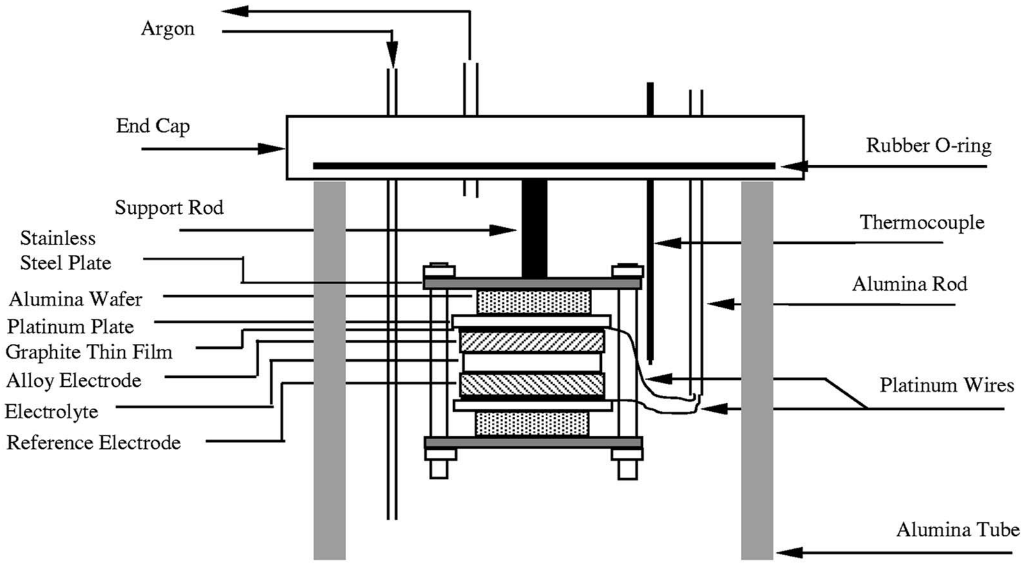

Fig. 2. Schematic diagram of the cell assembly.

used to electrically insulate the cell from its surroundings. A Chromel–Alumel thermocouple placed within 5 mm from the electrolyte was used to control furnace temperature. Two platinum wires were spot welded to the platinum plates. These wires were used as electrical leads to the high input impedance electrometer that measures the cell voltage.

Reproducibility of the results was confirmed by temperature cycling during heating and cooling. Cell reversibility was checked by applying small external currents and checking if the cell voltage returned to its original values.

3. Results and discussion

In each run, the cell was equilibrated at the desired temperature in the range of 820–900 K. The equilibrium cell voltage and temperature were both recorded. For every experiment, the cell voltage varied linearly with temperature. The straight line fit of the experimental data using the least-square technique for all the alloys is presented in Table 1 along with those of Samokhval et al. [5]. Fig. 3 shows the experimental results of two runs for two alloy compositions ($x_{\mathrm{Al}} = 0.479$ and 0.736). Excellent agreement can be seen between the results of the sets of experiments for each alloy. This agreement suggests that this method has good reproducibility and thus the data generated are reliable.

The experimental results for all the alloys studied in the present work along with those of Samokhval et al. [5] are presented in Fig. 4. The cell voltage decreases slightly with increase in temperature. The figure also indicated that in most of the alloys the cell voltage decreases with increases in the aluminum content. The alloy containing 99 atom percent aluminum showed an EMF value of 0.5 mV and was independent of temperature. The partial Gibbs energy of the aluminum was calculated using the Nernst equation:

$$\Delta \bar{G}_{\mathrm{Al}} = -nFE \tag{1}$$

where $n = 3$ and $F = 23\,060.54$ cal/mol V and E is the cell voltage measured for each alloy at each temperature. The partial Gibbs energy of aluminum is given by the following equation:

$$\Delta \bar{G}_{\mathrm{Al}} = RT \ln \left(\frac{a_{\mathrm{Al}}}{a_{\mathrm{Al(s)}}} \right) \tag{2}$$

Since the activity of pure aluminum in its solid state is taken as unity, the activity of aluminum in the alloy can be determined as follows:

$$a_{\mathrm{Al}} = \exp\left(\frac{\Delta \bar{G}_{\mathrm{Al}}}{RT} \right) = \exp\left(\frac{-nFE}{RT} \right) \tag{3}$$

Table 1
Summary of results obtained in the present work along with those of Samokhval et al. [5]

Composition, x_{Al}	E (mV) $= a + bT$	Source
0.055	$484.10 - 0.183T$	Samokhval et al.
0.078	$464.60 - 0.177T$	Samokhval et al.
0.101	$389.40 - 0.117T$	Samokhval et al.
0.126–0.224	$277.10 - 0.023T$	Samokhval et al.
0.250	$305.70 - 0.066T$	Samokhval et al.
0.268	$364.00 - 0.135T$	Samokhval et al.
0.289	$328.00 - 0.099T$	Samokhval et al.
0.313	$273.23 - 0.0747T$	This work
0.329	$228.60 - 0.032T$	Samokhval et al.
0.365–0.495	$205.90 - 0.0317T$	Samokhval et al.
0.479	$219.69 - 0.0914T$	This work
0.5	$149.30 - 0.00731T$	Samokhval et al.
0.647	$217.85 - 0.126T$	This work
0.736	$193.42 - 0.1055T$	This work

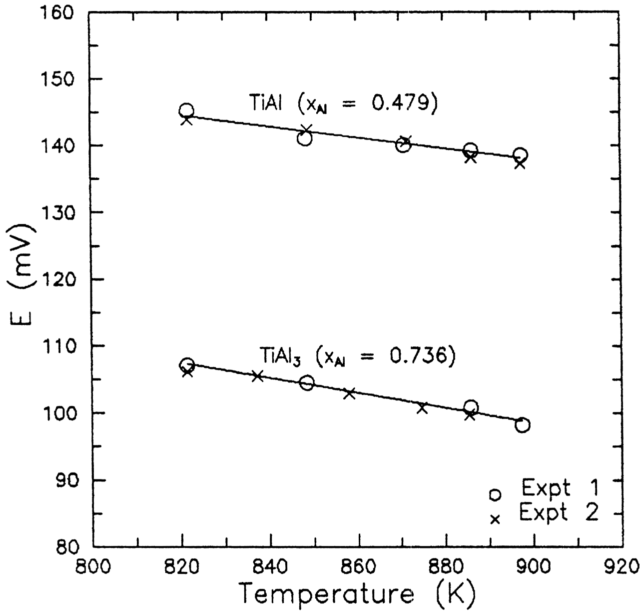

Fig. 3. Measured EMF vs. temperature for two alloys.

Table 2
Calculated thermodynamic properties of the Ti–Al system at 850 K

x_{Al}	Log γ_{Al}	Log γ_{Ti}	ΔG^M, kJ/mol	ΔG^E, kJ/mol
0.000	−4.5849	0.000	0.000	0.000
0.055	−4.5849	−0.0004	−5.6152	−4.1101
0.120	−4.1169	−0.0455	−11.2841	−8.6909
0.220	−4.1169	−0.0499	−19.0954	−15.3717
0.313	−2.5951	−0.6088	−24.6801	−20.2499
0.350	−2.2061	−0.8046	−25.6510	−21.0754
0.479	−2.2061	−0.8247	−29.0570	−24.1652
0.560	−1.7184	−1.3537	−30.1991	−25.3515
0.647	−1.7813	−1.2838	−30.7174	−26.1288
0.650	−1.6584	−1.5105	−30.7201	−26.1445
0.736	−1.7151	−1.4628	−30.8885	−26.8460
0.750	−1.7206	−1.4469	−30.8593	−26.8852
0.990	−0.0045	−11.5718	−2.3513	−1.9555

Furthermore, the activity coefficient of aluminum can be calculated as follows:

$$\gamma_{Al} = \frac{1}{x_{Al}} \exp\left(\frac{-nFE}{RT}\right) \quad (4)$$

The activity coefficient of titanium in the alloy can be calculated using the Gibbs–Duhem equation and the 'α' function as follows:

$$\ln \gamma_{Ti} = x_{Al} x_{Ti} \left(\frac{\ln \gamma_{Al}}{x_{Ti}^2}\right) - \int_{1}^{x_{Ti}} \left(\frac{\ln \gamma_{Al}}{x_{Ti}^2}\right) dx_{Ti} \quad (5)$$

Table 2 lists the calculated thermodynamics properties of the Ti–Al system at 850 K. Fig. 5 shows the negative logarithm of the activity coefficient of each element as a function of the aluminum content in the alloy. For low aluminum content, the activity coefficient of titanium in the alloy is near 1 while the activity coefficient of

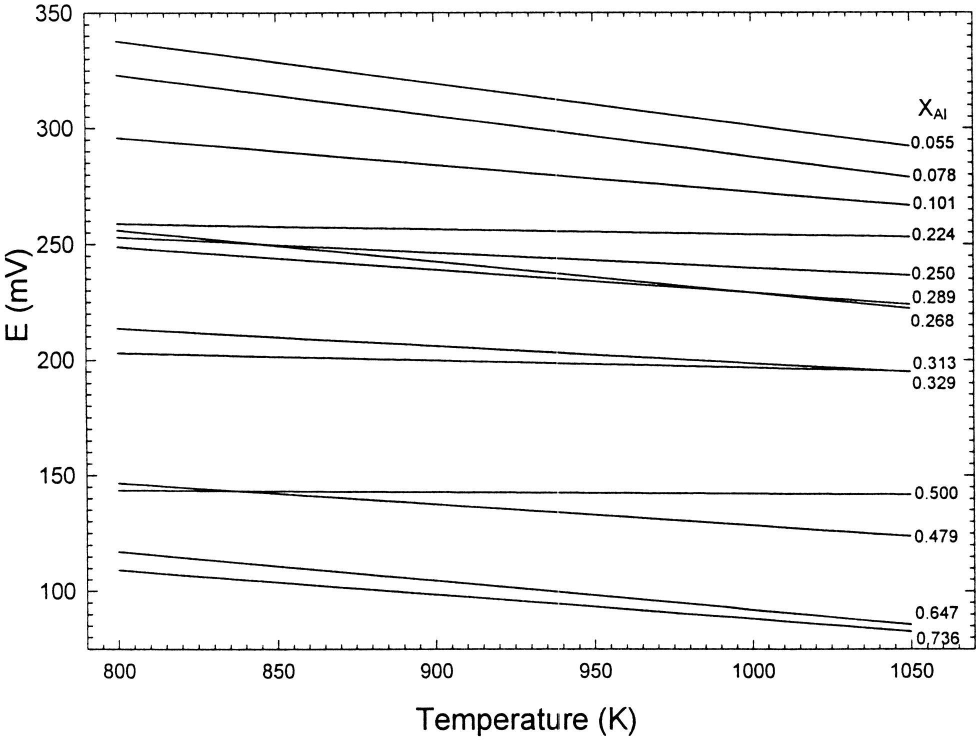

Fig. 4. Measured EMF vs. temperature for all compositions.

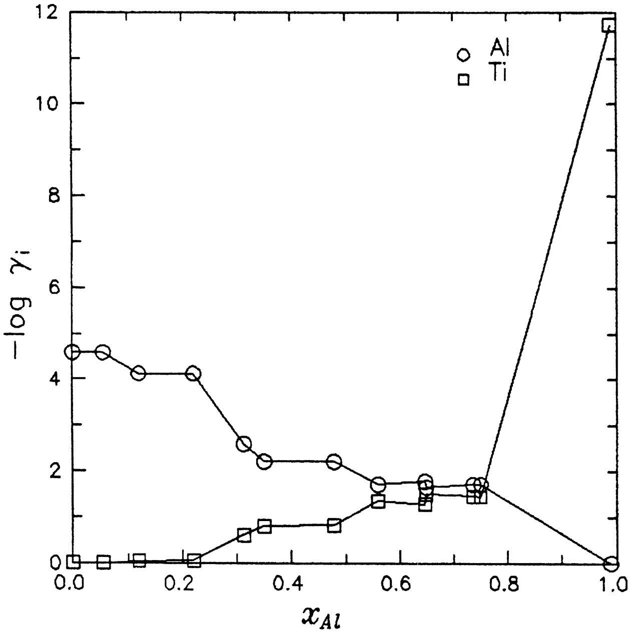

Fig. 5. Activity coefficients of Ti and Al as a function of x_{Al} at 850 K.

aluminum is small ($<10^{-4}$). On the other hand for high aluminum content, the activity coefficient of aluminum is near 1 while that of titanium is very small ($<10^{-10}$). The activity coefficients of aluminum and titanium in the alloys whose compositions correspond to the intermetallic compounds ranging from Ti_3Al to $TiAl_3$ are in the range of 10^{-1}–10^{-3}. These results show a negative deviation from ideality for both the elements indicating a strong attractive interaction between aluminum and titanium.

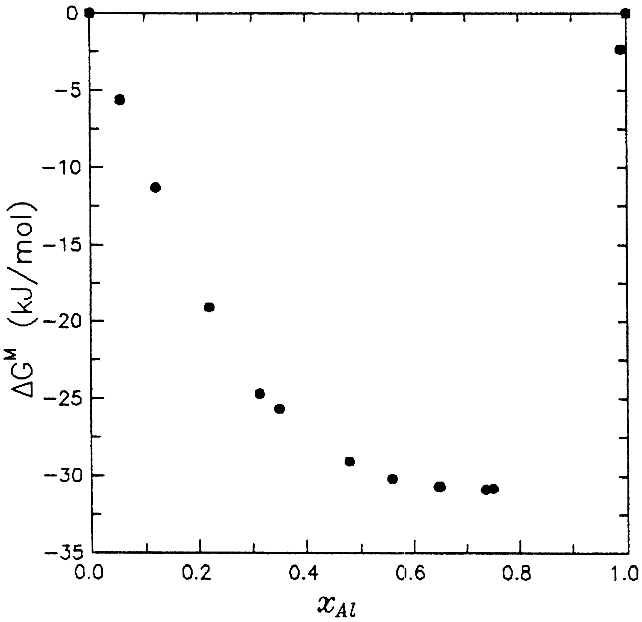

Fig. 6. Integral Gibbs energy of mixing of the Ti–Al system as a function of x_{Al} at 850 K.

From Eq. (5), at a given temperature and composition, the partial Gibbs energy of titanium in the alloy was calculated as follows:

$$\Delta \bar{G}_{Ti} = RT \ln a_{Ti} = RT \ln (\gamma_{Ti} x_{Ti}) \quad (6)$$

From the alloy composition, Gibbs energy of mixing of the alloy can be calculated using Eqs. (1) and (6):

$$\Delta G^M = x_{Al} \Delta \bar{G}_{Al} + x_{Ti} \Delta \bar{G}_{Ti} \quad (7)$$

Fig. 6 shows Gibbs energy of mixing as a function of aluminum content in the alloy at 850 K. Since these values are negative for all compositions, any mixture of titanium and aluminum at 850 K would spontaneously react and readily form an alloy. Increasing the aluminum content would form more stable intermetallics. The most stable intermetallic compound seemed to be $TiAl_3$ while the least stable was Ti_3Al.

4. Conclusions

Thermodynamic properties of Ti–Al system were determined using an EMF method. Activities and activity coefficients of Ti and Al in the system were calculated. Large negative deviation from ideal behavior was observed for both elements. Other thermodynamic properties such as $\Delta \bar{G}_{Al}$, $\Delta \bar{H}_{Al}$, $\Delta \bar{S}_{Al}$, $\Delta \bar{G}_{Ti}$, $\Delta \bar{H}_{Ti}$, $\Delta \bar{S}_{Ti}$, ΔG^M, ΔH^M, ΔS^M, ΔG^{ex}, ΔH^{ex}, and ΔS^{ex} can be calculated. For any mixture of titanium and aluminum, an alloy is thermodynamically expected to readily form. The most stable intermetallic in the Ti–Al system at 850 K is $TiAl_3$. Cell voltage linearly decreases with increasing temperature. For most compositions, increasing the Al content in the alloy reduced the cell voltage.

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